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(54) OXYMETHYLENE (CO)POLYMER COMPOSITION

(57) Abstract:

PROBLEM TO BE SOLVED: To obtain a composition which can give a molding having reduced loss of weight at high temperatures, coloration and the elution of formaldehyde and being excellent in fatigue resistance, abrasion properties and dimensional stability by using an oxymethylene (co)polymer and a hydrazide compound as the essential components.

SOLUTION: This composition comprises an oxymethylene

(co)polymer being desirably a copolymer of a cyclic oligomer of formaldehyde with a 2-6 C cyclic ether and/or a cyclic acetal, more desirably a trioxane/ethylene oxide copolymer comprising 90-99 mol.% recurring units of the formula: -OCH₂- and 1-10 mol.% monomer units of the formula: -OCH₂CH₂- and derived from ethylene oxide and 0.01-5 mass %, based on the total of both, hydrazide compound (e.g. adipic acid dihydrazide) being desirably at least one 4-12 C aliphatic dihydrazide.

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DETAILED DESCRIPTION

[Detailed Description of the Invention]

[0001]

[Field of the Invention] This invention relates to the oxy-methylene (***) polymer constituent excellent in thermal stability.

[0002]

[Description of the Prior Art] As a heat stabilizing agent of an oxy-methylene (**) polymer, conventionally Cyanoguanidine, Amidines, such as cyano-3-methylguanidine, a dicyandiamide, guanidine, and aminoguanidine; A melamine, Triazine;N-phenyl ureas, such as benzoguanamine and N-phenyl melamine, Ureas, such as an N and N'-diphenylurea; Phenylhydrazine, a diphenyl hydrazine, Hydrazines, such as a semicarbazone; Independent or copolymers, such as nylon 6, nylon 6, and 6, or independent or thing; which uses amide compounds, such as a copolymer, as an indispensable component of a polyamide guided from a divalent carboxylic acid and diamines, such as an adipic acid, a sebacic acid, and dimer acid, is known (for example, JP, 63-112650, A --) JP, 63-63741, A.

[0003]

[Problem(s) to be Solved by the Invention] The depolymerization from an end group tends to break out, and since an oxy-methylene (**) polymer has the mass loss in quantity by the hot pyrolysis; and large coloring, it is performing end group processing for stabilization. Although making the oxy-methylene (**) polymer which carried out end group processing contain the above-mentioned nitrogen-containing compound system heatproof improver is known in order to raise thermal stability furthermore, it is still dissatisfied.

[0004]

[Means for Solving the Problem] As a result of this invention person's etc. examining wholeheartedly the polymer constituent which solves the above-mentioned technical problem, the oxy-methylene (**) polymer containing a specific nitrogen-containing compound found out that there was little mass loss in quantity also in an elevated temperature, and there was little coloring, and reached this invention. That is, this invention is a Plastic solid of (A) with which the oxy-methylene (**) polymerization body composition object which makes an oxy-methylene (**) polymer (A) come to contain a hydrazide compound (B) as an indispensable component, and a list come to fabricate ** (A) in the heating melting condition under existence of ** (B).

[0005]

[Embodiment of the Invention] As an oxy-methylene (**) polymer (A) in this invention According to any one or more sorts of the trioxane which is formaldehyde or its annular oligomer, or tetra-oxane, and the need These, copolymerizable ethylene oxide and propylene oxide, 1, 2-butylene oxide, The cyclic ether and/or the annular acetals of carbon numbers 2-6, such as 1 and 3-dioxolane the content of an oxy-

methylene unit [as opposed to / are the oxy-methylene homopolymer or oxymethylene copolymer of a polymerization catalyst which is made to carry out the bottom polymerization of existence, and is obtained, and / the total quantity of an oxyalkylene unit] -- usually -- more than 80 mol % -- the thing beyond 90 mol % is mentioned preferably. Things desirable [among these] are the annular oligomer of formaldehyde, the cyclic ether of the above-mentioned carbon numbers 2-6, and/or a copolymer with an annular acetal, and especially a desirable thing is a formula. - It is OCH₂. - It is a trioxane-ethylene oxide copolymer containing 90-99 mol % of repeating units, and 1-10 mol % of monomeric units of formula-OCH₂CH₂- guided from ethylene oxide. The copolymer is excellent in thermal resistance.

[0006] The above-mentioned oxy-methylene (**) polymer (A) is obtained by the well-known approach. For example, cyclic ether or annular acetals, such as a trioxane, ethylene oxide, and dioxolane, are mixed, 3 ****-ized boron coordination compounds, such as % of a 0.01-0.1-mol 3 ****-ized boron diethylether complex and a 3 ****-ized boron methanol complex, are added to a trioxane, and a polymerization is carried out under existence of a solvent or un-existing. Reaction temperature is usually 50-90 degrees C, and 10 minutes - reaction-time 5 hours. Solvents, such as a cyclohexane, toluene, and benzene, are suitable for a solvent. A polymerization reaction usually stops by adding trivalent organic phosphorous compound; such as JP,60-90250,A, such as fatty amine; bis(2, 2, 6, and 6-tetramethyl-4-piperidyl) OGIZA rates, such as tree n butylamine and triethylamine, or hindered amine; triphenyl phosphine given in JP,63-63741,A, a diethyl butyl phosphine, phosphorous acid triphenyl, and phosphorous acid tritolyl. Since the end after a polymerization has the hydroxyl which is easy to disassemble, various end stabilizing treatment is usually performed. For example, the approach of carrying out terminal modification of the end hydroxyl of a polymer with reactant compounds, such as an acetic anhydride and an isocyanate compound, and the approach of making it stability by hydrolysis are learned. However, when the above-mentioned trivalent organic phosphorous compound is added as a halt agent, an end stabilizing treatment process is unnecessary and desirable.

[0007] from the usefulness of the Plastic solid with which the number average molecular weight of the oxy-methylene (**) polymer (A) used for this invention is obtained -- desirable -- 5,000-200,000 -- it is 10,000-100,000 more preferably.

[0008] As a hydrazide compound (B) in this invention, the hydrazide compound guided from the monocarboxylic acid of aliphatic series or aromatic series, dicarboxylic acid, or hydroxy acid of carbon numbers 1-20 is mentioned. As an example, KARUBO hydrazide, propionic-acid hydrazide, butanoic acid hydrazide, Dodecanoic acid hydrazide, tetradecane acid hydrazide, hexadecane acid hydrazide, Aliphatic series, such as octadecanoic acid hydrazide and salicylic-acid hydrazide, or aromatic series mono-hydrazide; Succinic-acid dihydrazide, Adipic-acid dihydrazide, pimelic-acid dihydrazide, suberic-acid dihydrazide, Aliphatic series, such as azelaic-acid dihydrazide, sebacic-acid dihydrazide, dodecane JIOHIDORAJIDO, and isophthalic acid dihydrazide, or aromatic series dihydrazide; is

mentioned, and these may be used independently or may use two or more sorts together. Things desirable [among these] are aliphatic series dihydrazide of carbon numbers 4-12, such as the adipic-acid dihydrazide from the magnitude of a heat stabilization effect, pimelic-acid dihydrazide, suberic-acid dihydrazide, azelaic-acid dihydrazide, sebacic-acid dihydrazide, and dodecane JIOHIDORAJIDO. By adding (B), there are few falls of the coloring-proof nature at the time of the elevated temperature of (A), and reduction in mass decreases.

[0009] the content of the above (B) in the oxy-methylene (**) polymer constituent of this invention -- the sum total mass of (A) and (B) -- being based -- desirable -- 0.01 - 5 mass % -- more -- desirable -- 0.02 - 2 mass % -- it is 0.02 - 1 mass % especially preferably. If the content of (B) has a large reduction of the mass under an elevated temperature and exceeds 5 mass % under by 0.01 mass %, coloring of an oxy-methylene (**) polymer will become large.

[0010] The polymer (**) constituent of this invention the specified quantity of the oxymethylene copolymer (A) obtained by the above-mentioned well-known approach A hydrazide compound (B), The well-known heat-resistant improver besides additive (C) [which is others by the need; An antioxidant, The stabilizing agent of others, such as an ultraviolet ray absorbent; with], such as inorganic bulking agent; pigment; antifungal agent;, such as lubricant; glass fibers, such as a silica, a wax, and fatty acid ester, talc, and a mica It can obtain with a mixer or extruders, such as a roll mold, the Banbury mold, and a Henschel type, by carrying out homogeneity mixing by the usual method of mixing or kneading. It is the approach of carrying out preliminary mixing of (B) and other additives (C), and introducing this reserve mixture into an oxy-methylene (**) polymer (A) by the supply throat of an extruder preferably, among these approaches. Other above-mentioned additives (C) can be blended in the range to 5 mass % of the total mass of the constituent of this invention.

[0011] As an example of other above-mentioned well-known heat-resistant improvers Cyanoguanidine, cyano-3-methylguanidine, a dicyandiamide, Amidines, such as guanidine and aminoguanidine; A melamine, benzoguanamine, Triazine, such as N-phenyl melamine; N-phenyl urea, N, Ureas, such as an N'-diphenylurea; Phenylhydrazine, a diphenyl hydrazine, Hydrazines, such as a semicarbazone; Independent or copolymers, such as nylon 6, nylon 6, and 6, Or amide compound; guided from a divalent carboxylic acid and diamines, such as an adipic acid, a sebacic acid, and dimer acid, such as independent or a copolymer of a polyamide, is mentioned. It is indicated by JP,62-190248,A, JP,63-112650,A, JP,63-63741,A, etc. the loadings in the case of using together (B) and these well-known nitrogen-containing compound system heatproof improvers (C1) -- (A) from the heat-resistant improvement effectiveness, and (B) -- and (C1) (B) based on sum total mass -- and (C1) a content -- desirable -- 0.01 - 5 mass % -- it is 0.02 - 2 mass % more preferably. Moreover, as a well-known heat-resistant improver, the alkali-metal salt or alkaline-earth-metal salts of an inorganic acid, such as the aliphatic series monochrome of carbon numbers 2-9, JI, tricarboxylic acid; aroma aliphatic series of carbon numbers 7-9 or aromatic carboxylic acid, a

hydroxide, a hydrochloric acid, and a sulfuric acid, are also mentioned to except (C1).

[0012] As an example of the above-mentioned anti-oxidant, they are phenols, such as G beta-naphthol, n-butyl-para aminophenol, isobutyl-para aminophenol, phenyl salicylate, and para hydroxydiphenyl, 2,2-methylene bis (4-methyl-t-butylphenol), and a hexamethylene glycol screw (JP,60-11550,A, such as 3 and 5-G t-butyl-4-hydroxy hydronium cinnamate, and steric hindrance nature phenols given in JP,60-902500,A are mentioned.).

[0013] After carrying out beating of the constituent of this invention mechanically and making it into a grain, a chip, a flake, or powder, it is fabricated in the heating melting condition by the desired configuration using the usual briquetting machines, such as injection molding or extrusion molding, press forming, casting, compression molding, blow molding, inflation processing, calendering, and T-die processing. Since the constituent of this invention has good thermal stability, there is little reduction in mass also at the time of heating melting, and it has little coloring. Moreover, the thermal stability improved similarly can be obtained also by the approach of adding (B) to (A) at the time of heating melting of (A).

[0014] The acquired Plastic solid is used for the application of an electron and an electrical part, autoparts, opportunity components, building materials and a pipe fitting, a car and a vessel ingredient, a container, daily necessities, etc.

[0015]

[Example] Hereafter, although an example explains this invention further, this invention is not limited to this. % is [following] mass %. The section is the mass section.

[0016] The trioxane 9000 section (100 mols) was taught to the kneader who has the impeller of 12 examples, and it heated and dissolved at 60 degrees C. The ethylene oxide 220 section (five mols) and the 3 ****-ized boron diethylether complex (25% of contents) 8.5 section were added, and the polymerization was performed for 30 minutes to the bottom of churning. The rough oxymethylene copolymer 9000 section was obtained. this, the triphenyl phosphine 0.8 section was added in the methylene copolymer 1000 section, and homogeneity mixing was carried out. [rough] The adipic-acid dihydrazide 3 section, 2, and 2'-methylenebis (4-methyl-t-butylphenol) 5 section and the calcium-hydroxide 1 section were added to this, with the lab PURASUTO mill, it kneaded for 30 minutes at 190 degrees C under nitrogen-gas-atmosphere mind, and the oxymethylene copolymer constituent of this invention was obtained.

[0017] Instead of the adipic-acid dihydrazide of two to example 6 example 1, sebacic-acid dihydrazide (example 2), dodecane JIOHIDORAJIDO (example 3), isophthalic acid dihydrazide (example 4), propionic-acid hydrazide (example 5), and dodecanoic acid hydrazide (example 6) were added, same actuation was performed, and the oxymethylene copolymer constituent of this invention was obtained.

[0018] Instead of the adipic-acid dihydrazide of one to example of comparison 4 example 1, the polyamide (example 4 of a comparison) guided from additive-free (example 1 of a comparison) and cyanoguanidine (example 2 of a comparison), benzoguanamine (example 3

of a comparison), and a dimer acid-hexamethylenediamine was added respectively, homogeneity kneading was carried out similarly, and the oxymethylene copolymer constituent was obtained.

[0019] The following approach estimated the oxymethylene copolymer constituent of example of trial 1 examples 1-6, and the examples 1-4 of a comparison. The result is shown in Table 1.

[0020]

[Table 1]

実施例	MFI	質量減少率%	着色防止性	抽出ホルムアルデヒド量ppm	
				加熱前	加熱後
実施例1	8.3	1.2	70	110	560
実施例2	8.4	1.1	72	120	650
実施例3	8.4	1.3	71	110	680
実施例4	8.8	1.6	67	130	780
実施例5	8.9	1.6	68	130	720
実施例6	8.9	1.7	68	140	730
比較例1	18.5	12.1	58	450	2350
比較例2	10.2	3.2	60	280	1720
比較例3	9.9	3.1	61	270	1650
比較例4	11.2	2.9	61	230	1680

[0021] Melt flow index (MFI) : It measured with the extrusion plastometer. A Measuring condition is temperature. 190 degrees C, load The flow rate per 10 minutes shows by 2160g. A smaller numeric value shows that there is little decomposition.

Mass percentage reduction: The sample was heated in 230-degree C oven, and the mass percentage reduction of the 60 minutes after was measured. A smaller numeric value is excellent.

Coloring tightness: It heated in oven for 230 degree-Cx 60 minutes, and the brightness by Hunter was measured. A larger numeric value is excellent.

The amount of extract formaldehyde: 100g of samples of the oxymethylene copolymer constituent of the back before heating in oven with a temperature of 230 degrees C for 60 minutes is added to 100ml distilled water, and reflux heating is carried out by boiling temperature for 60 minutes. 0.1-N potassium hydroxide solution neutralizes an extract solution, and Last pH is recorded. 50ml of 1-N

sodium-sulfite solutions is added in the neutralized solution, and it titrates with 0.1-N sulfuric acid until it returns to the first pH subsequently to before recorded. The value of the amount of extract formalin is computed by the degree type. A smaller numeric value is excellent.

The amount of formaldehyde (ppm) = $(TxNx30000)$ the inside of a /W type, T= sulfuric-acid titration value (ml)

Normality W= sample mass of N= sulfuric acid (g)

[0022]

[Effect of the Invention] The oxy-methylene (**) polymer constituent of this invention has little reduction of hot mass, and there is little coloring. There is little formaldehyde extracted and it has become the polymer presentation which is hard to decompose with heat. Since it has the above-mentioned effectiveness, the Plastic solid demonstrates the outstanding fatigue strength, a wear property, and dimensional stability; and is useful for applications, such as an electron and an electrical part, and autoparts, as a Plastic solid of metal components substitution.

CLAIMS

[Claim(s)]

[Claim 1] The oxy-methylene (**) polymerization body composition object which makes an oxy-methylene (**) polymer (A) come to contain a hydrazide compound (B) as an indispensable component.

[Claim 2] The constituent according to claim 1 whose hydrazide compound (B) is aliphatic series dihydrazide of one or more sorts of carbon numbers 4-12.

[Claim 3] The constituent according to claim 1 or 2 whose content of (B) is 0.01 - 5 mass % based on the sum total mass of (A) and (B).

[Claim 4] Claims 1-3 whose (A) is the annular oligomer of formaldehyde, the cyclic ether of carbon numbers 2-6, and/or a copolymer with an annular acetal are the constituents of a publication either.

[Claim 5] The Plastic solid of (A) with which it comes to fabricate an oxy-methylene (**) polymer (A) in the heating melting condition under existence of a hydrazide compound (B).
